

Studies on the Stabilities of Some Mixed Ligand Complexes of Lanthanide(III) Ions

BHAWNA VARSHNEY and K.C. GUPTA*

*Department of Chemistry
B.S.A. College, Mathura-281 004, India*

Ternary complexes of lanthanides with CPTA as primary and quinaldic acid as a secondary ligand having the general formula [M-CPTA-quinaldic acid] where M = La(III), Sm(III), Eu(III), Gd(III) and Dy(III) have been described potentiometrically at different temperatures and at constant ionic strength $\mu = 0.2$ M (KNO₃) using the modified Irving and Rossotti's method. The thermodynamic parameters for the formation of the complex [M-CPTA-quinaldic acid] have also been calculated. The stability constants show the following order



Key Words: Stability constant, Free energy, Enthalpy, Entropy.

INTRODUCTION

The metal ligand stability constants of transition metal ions with CPTA as primary ligand have been reported by Gupta *et al.*^{1,2} but in our earlier publication, the studies on mixed ligand complexes of some lanthanide ions with CPTA as primary ligand are also reported^{3,4}.

The present investigation involves the determination of mixed ligand stability constants of La(III), Sm(III), Eu(III), Gd(III) and Dy(III) with CPTA and quinaldic acid at 25, 35 and 45°C. The modified method of Irving and Rossotti^{5,6} has been applied to study the formation constants.

The formation of mixed ligand complex in a solution containing M, A and B in 1 : 1 : 1 ratio takes place in the following two steps:



The reaction $\text{M} + \text{A} \rightleftharpoons \text{MA}$ takes place at lower pH and is stable at higher pH and thus for ternary complexes the equilibrium constant is

$$K_{\text{MAB}}^{\text{MA}} = \frac{[\text{MAB}]}{[\text{MA}][\text{B}]}$$

where A is primary and B is secondary ligand.

*Address for correspondence: Dr. K.C. Gupta, 508, Radhika Vihar, Mathura-281 004, India

EXPERIMENTAL

CPTA (Matheson, Coleman and Bell Co.) and all other chemicals used were BDH reagents of AR grade with the purity of 99.99%.

The solutions of metal nitrates were prepared by dissolving respective metal oxides in minimum amount of AR HNO_3 . Then the solutions were filtered through G-4 crucible of sintered glass and metal ions were estimated as per standard methods⁷. CPTA solution was prepared in conductivity water by dissolving calculated & weighed quantity of CPTA in a volumetric flask. In the same pattern quinaldic acid solution was prepared.

The potentiometric titrations were carried out with the help of digital Systronics pH-meter, model 335 with accuracy (± 0.01 pH units) at 25, 35 and 45°C ($\pm 0.1^\circ\text{C}$).

The initial volume of each solution to be titrated was kept 50 cc and the ionic strengths (μ) were kept at 0.2 M with KNO_3 . The solutions were titrated against 0.2 M KOH at different temperatures. The following sets of solutions were prepared

(A) 0.02 M HNO_3 + 0.18 M KNO_3 .

(B) 0.02 M HNO_3 + 0.002 M quinaldic acid + 0.178 M KNO_3 .

(C) 0.02 M HNO_3 + 0.002 M metal nitrate + 0.002 M CPTA + 0.176 M KNO_3 .

(D) 0.02 M HNO_3 + 0.002 M metal nitrate + 0.002 M CPTA + 0.002 M quinaldic acid + 0.174 M KNO_3 .

The solutions were thoroughly shaken and were allowed to equilibrate by keeping them for 1 h. Each of the solutions was titrated with standard alkali solution (0.2 M KOH) at fixed temperature.

RESULTS AND DISCUSSION

From the above described method, four titration curves obtained are referred to as:

(a) Acid titration curve, (b) Secondary ligand titration curve, (c) Primary complex titration curve and (d) Mixed ligand complex titration curve.

An observation of mixed ligand system shows that the mixed ligand curve displaces from binary complex curve indicating the interaction between the primary complex and the secondary ligands. A typical representative plot of pH vs. alkali added is shown in Fig. 1 for La^{3+} CPTA-quinaldic acid system.

The primary complex curve (c) and mixed ligand curve (d) overlap each other up to pH 3.75. This indicates that in this pH range, where primary ligand combines with metal, combination of secondary ligands does not take place. Curve (d) diverges from curve (c) after pH 3.75 showing that the combination of secondary ligand with primary complex starts. The horizontal distances (V_2) between curves (a) and (b), (V_3) between curves (c) and (d) indicate the proton released due to self-dissociation of secondary ligand plus the release of proton due to the

formation of mixed ligand complex. Thus $(V_3 - V_2)$ accounts for the total protons released due to formation of the mixed ligand complex.

The dissociation constants (pK values) of the ligands were obtained from the formation curves obtained by plotting pH vs. $\bar{n}H$. The experimental pK values are in agreement with the literature values⁸. The values of \bar{n} (the average number of secondary ligand molecules attached to primary complex) were calculated from the equation^{3,9}

$$\bar{n} = \frac{(V_3 - V_2)(N + E^\circ)}{(V_0 + V_1)\bar{n}H T_{cm}^\circ}$$

where, T_{cm}° = total concentration of metal ion in solution, N = normality of alkali, E° = initial strength of the acid in the system, V_0 = total volume of the mixture taken initially, V_1 = the volume of alkali required in the titration of mineral acid (mix. A), V_3 and V_2 are the differences in the volumes of alkali added between curves (d) and (c), and (b) and (a) respectively (Fig. 1) at the same pH, $\bar{n}H$ = the average number of protons attached to secondary ligand at the same pH.

The pL values were calculated at $\bar{n} = 0.5$ from the equation

$$\{pL = \log \left\{ \frac{\sum_{n=0}^{\infty} \beta_n^H (1/\text{antilog } \beta)^n}{T_{Cl}^\circ - \bar{n}T_{cm}^\circ} \left(\frac{V_0 + V_4}{V_0} \right) \right\}$$

where, β_n^H = overall practical proton ligand stability constant and V_4 is the volume of alkali required for curve (d) at the same pH and summarized in Table-1. The error limit is 0.08 log units.

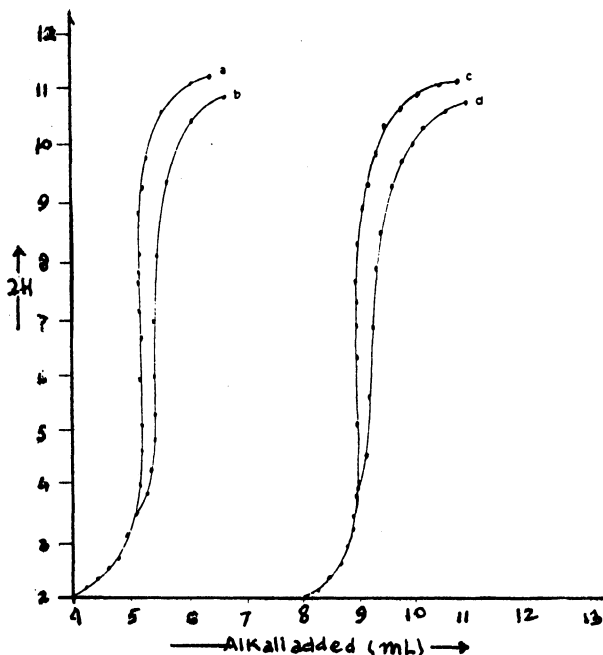


Fig. 1. Titration curve corresponding to La^{3+} -CPTA-quinaldic acid system

- (a) Acid titration curve, (b) Secondary ligand titration curve,
 (c) Primary complex titration curve, (d) Mixed ligand complex titration curve,

The thermodynamic parameters, viz., change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also determined by the following equations:

$$\Delta G^\circ = -2.303RT \log K$$

$$\Delta H^\circ = \frac{2.303RT_1T_2 \log(\beta_2 - \beta_1)}{(T_2 - T_1)}$$

$$\Delta S^\circ = [\Delta H^\circ - \Delta G^\circ]/T$$

where T = absolute temperature, R = gas constant, log K = formation constant of the mixed ligand species, β_1 and β_2 are the stability constant at temperatures T_1 and T_2 respectively.

The thermodynamic parameters determined by these equations are summarized in Table-1. The stability constants of the metal ions follow the order:



The above trend is further confirmed by the values of ΔG° obtained during the course of the investigation.

TABLE-1
STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS
OF MIXED LIGAND COMPLEXES AT DIFFERENT TEMPERATURES
($\mu = 0.2 \text{ M KNO}_3$)

System	Temp. (°C)	$\log K_{\text{MAB}}^{\text{MA}}$	ΔG° (kcal mol ⁻¹)	ΔH° (kcal mol ⁻¹)	ΔS° (cal mol ⁻¹)
La ³⁺ -CPTA-quinaldic acid	25	3.670	-4.987	4.541	31.94
	35	3.755	-5.274		
	45	3.880	-5.626		
Sm ³⁺ -CPTA-quinaldic acid	25	3.665	-4.980	5.838	36.39
	35	3.860	-5.421		
	45	3.935	-5.706		
Eu ³⁺ -CPTA-quinaldic acid	25	4.120	-5.599	2.811	28.24
	35	4.200	-5.899		
	45	4.250	-6.163		
Gd ³⁺ -CPTA-quinaldic acid	25	4.250	-5.775	7.459	44.18
	35	4.275	-6.004		
	45	4.595	-6.663		
Dy ³⁺ -CPTA-quinaldic acid	25	3.620	-4.919	4.541	31.84
	35	3.790	-5.323		
	45	3.830	-5.554		

Error limits ± 0.08 log units

ACKNOWLEDGEMENT

The authors are thankful to Pricipal, B.S.A. College, Mathura for providing necessary laboratory facilities.

REFERENCES

1. R. Agarwal and K.C. Gupta, *Nat. Acad. Sci. Letters*, **12**, 51 (1989).
2. K.C. Gupta and K. Shrinivasulu, *Nat. Acad. Sci. Letters*, **13**, 273 (1990).
3. S.K. Agarwal and K.C. Gupta, *Indian J. Chem.*, **27A**, 1008 (1988).
4. B. Singh, R.B. Gupta and K.C. Gupta, *Nat. Acad. Sci. Letters*, **17**, 137 (1994).
5. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904 (1954).
6. M.V. Chidambaram and P.K. Bhattacharya, *J. Inorg. Nucl. Chem.*, **32**, 3271 (1970).
7. A.I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, Longmans Green, London (1978).
8. Meites Luis, *Hand Book of Analytical Chemistry*, McGraw-Hill, New York (1982).
9. K.B. Yatsimirski and V.V.P. Vasile, *Instability Constants of Complex Compounds*, Pergamon Press, New York (1960).

(Received: 27 January 2003; Accepted: 1 May 2003)

AJC-3070